Median dual cell 1D

August 22, 2007

1 Equations

1.1 Mass conservation

$$\frac{\partial c_i}{\partial t} = -\vec{\nabla}.\vec{N}_i + R_i \tag{1}$$

with

$$\vec{N}_i = c_i\vec{v} - \sum_j D_{ij}\vec{\nabla}c_j - w_i c_i \vec{\nabla}U \tag{2}$$

1.2 Poisson's equation

$$\vec{\nabla}^2 U + \frac{F}{\epsilon}\sum_i z_i c_i = 0 \tag{3}$$

1.3 Butler-Volmer kinetics

$$v = k_{ox}\exp\left[\frac{\alpha_{ox} nF}{RT}(V-U)\right]c_{red} - k_{red}\exp\left[-\frac{\alpha_{red} nF}{RT}(V-U)\right]c_{ox} \tag{4}$$

2 Element matrix

2.1 Convection

2.1.1 Fluctuation in node

$$\Delta c_i^m = \int_{L^m} -\vec{v}.\vec{\nabla}c_i dL$$

2.1.2 Element contribution to fluctuation in node

$$\vec{\mathcal{V}}^1 = 3\vec{v}^1 + \vec{v}^2$$

$$\vec{\mathcal{V}}^2 = \vec{v}^1 + 3\vec{v}^2$$

$$\left\{ \begin{array}{c} \Delta c_i^1 \\ \Delta c_i^2 \end{array} \right\} = \frac{1}{8} \left[\begin{array}{cc} \vec{\mathcal{V}}^1.\vec{n}^1 & \vec{\mathcal{V}}^1.\vec{n}^2 \\ \vec{\mathcal{V}}^2.\vec{n}^1 & \vec{\mathcal{V}}^2.\vec{n}^2 \end{array} \right] \left\{ \begin{array}{c} c_i^1 \\ c_i^2 \end{array} \right\} \tag{5}$$

2.1.3 Example: binary electrolyte

$$\left\{ \begin{array}{c} \Delta c_A^1 \\ \Delta c_B^1 \\ \Delta U^1 \\ \Delta c_A^2 \\ \Delta c_B^2 \\ \Delta U^2 \end{array} \right\} = \left[\begin{array}{cccccc} V^{11} & 0 & 0 & V^{12} & 0 & 0 \\ 0 & V^{11} & 0 & 0 & V^{12} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ V^{21} & 0 & 0 & V^{22} & 0 & 0 \\ 0 & V^{21} & 0 & 0 & V^{22} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{array} \right] \left\{ \begin{array}{c} c_A^1 \\ c_B^1 \\ U^1 \\ c_A^2 \\ c_B^2 \\ U^2 \end{array} \right\} \tag{6}$$

with

$$V^{mn} = \frac{\vec{\mathcal{V}}^1.\vec{n}^1}{8}$$

2.2 Diffusion

2.2.1 Fluctuation in node

$$\begin{aligned} \Delta c_i^m &= \int_{L^m} \vec{\nabla}. \left(\sum_j D_{ij} \vec{\nabla} c_j \right) dL \\ &= -\int_{\partial L^m} \left(\sum_j D_{ij} \vec{\nabla} c_j \right) .d\vec{n} \end{aligned}$$

2.2.2 Element contribution to fluctuation in node

$$\vec{\mathcal{D}}_{ij}^1 = \left(D_{ij}^1 + D_{ij}^2 \right) \vec{n}^1$$

$$\vec{\mathcal{D}}_{ij}^2 = \left(D_{ij}^1 + D_{ij}^2 \right) \vec{n}^2$$

$$\left\{ \begin{array}{c} \Delta c_i^1 \\ \Delta c_i^2 \end{array} \right\} = -\frac{1}{2L} \sum_j \left[\begin{array}{cc} \vec{\mathcal{D}}_{ij}^1.\vec{n}^1 & \vec{\mathcal{D}}_{ij}^1.\vec{n}^2 \\ \vec{\mathcal{D}}_{ij}^2.\vec{n}^1 & \vec{\mathcal{D}}_{ij}^2.\vec{n}^2 \end{array} \right] \left\{ \begin{array}{c} c_j^1 \\ c_j^2 \end{array} \right\} \tag{7}$$

2.2.3 Example: binary electrolyte

$$\left\{ \begin{array}{c} \Delta c_A^1 \\ \Delta c_B^1 \\ \Delta U^1 \\ \Delta c_A^2 \\ \Delta c_B^2 \\ \Delta U^2 \end{array} \right\} = \left[\begin{array}{cccccc} D_{AA}^{11} & D_{AB}^{11} & 0 & D_{AA}^{12} & D_{AB}^{12} & 0 \\ D_{BA}^{11} & D_{BB}^{11} & 0 & D_{BA}^{12} & D_{BB}^{12} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ D_{AA}^{21} & D_{AB}^{21} & 0 & D_{AA}^{22} & D_{AB}^{22} & 0 \\ D_{BA}^{21} & D_{BB}^{21} & 0 & D_{BA}^{22} & D_{BB}^{22} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{array} \right] \left\{ \begin{array}{c} c_A^1 \\ c_B^1 \\ U^1 \\ c_A^2 \\ c_B^2 \\ U^2 \end{array} \right\} \tag{8}$$

with

$$D_{ij}^{mn} = -\frac{\vec{\mathcal{D}}_{ij}^m.\vec{n}^n}{2L}$$

2.3 Migration

2.3.1 Fluctuation in node

$$\begin{aligned} \Delta c_i^m &= \int_{L^m} \vec{\nabla}.\left(w_i c_i \vec{\nabla} U\right) dL \\ &= -\int_{\partial L^m} \left(w_i c_i \vec{\nabla} U\right).d\vec{n} \end{aligned}$$

2.3.2 Element contribution to fluctuation in node

Assume that w_i varies linearly.

$$\vec{\mathcal{M}}_i^1 = \vec{\mathcal{W}}_i^{11} c_i^1 + \vec{\mathcal{W}}_i^{12} c_i^2$$

$$\vec{\mathcal{M}}_i^2 = \vec{\mathcal{W}}_i^{21} c_i^1 + \vec{\mathcal{W}}_i^{22} c_i^2$$

$$\vec{\mathcal{W}}_i^{11} = \vec{\mathcal{W}}_i^{12} = \left(w_i^1 + w_i^2\right) \vec{n}^1$$

$$\vec{\mathcal{W}}_i^{21} = \vec{\mathcal{W}}_i^{22} = \left(w_i^1 + w_i^2\right) \vec{n}^2$$

$$\left\{ \begin{array}{c} \Delta c_i^1 \\ \Delta c_i^2 \end{array} \right\} = -\frac{1}{16L} \left[\begin{array}{cc} \vec{\mathcal{M}}_i^1.\vec{n}^1 & \vec{\mathcal{M}}_i^1.\vec{n}^2 \\ \vec{\mathcal{M}}_i^2.\vec{n}^1 & \vec{\mathcal{M}}_i^2.\vec{n}^2 \end{array} \right] \left\{ \begin{array}{c} U^1 \\ U^2 \end{array} \right\} \tag{9}$$

2.3.3 Example: binary electrolyte

$$\left\{ \begin{array}{c} \Delta c_A^1 \\ \Delta c_B^1 \\ \Delta U^1 \\ \Delta c_A^2 \\ \Delta c_B^2 \\ \Delta U^2 \end{array} \right\} = \left[\begin{array}{cccccc} 0 & 0 & M_A^{11} & 0 & 0 & M_A^{12} \\ 0 & 0 & M_B^{11} & 0 & 0 & M_B^{12} \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & M_A^{21} & 0 & 0 & M_A^{22} \\ 0 & 0 & M_B^{21} & 0 & 0 & M_B^{22} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{array} \right] \left\{ \begin{array}{c} c_A^1 \\ c_B^1 \\ U^1 \\ c_A^2 \\ c_B^2 \\ U^2 \end{array} \right\} \tag{10}$$

with

$$M_i^{mn} = -\frac{\vec{\mathcal{M}}_i^m.\vec{n}^n}{16L}$$

2.4 Homogeneous reactions

2.4.1 Fluctuation in node

$$R_i = \sum_r s_{i,r} v_r$$

- Monomolecular

$$v = kc_j$$

$$\Delta c_i^m = \int_{L^m} kc_j dL$$

- Bimolecular

$$v = kc_j c_k$$

$$\Delta c_i^m = \int_{L^m} kc_j c_k dL$$

2.4.2 Element contribution to fluctuation in node

Assume that k varies linearly.

- Monomolecular

$$\mathcal{H}_j^{11} = 7k^1 + 2k^2$$

$$\mathcal{H}_j^{12} = 2k^1 + k^2$$

$$\mathcal{H}_j^{21} = k^1 + 2k^2$$

$$\mathcal{H}_j^{22} = 2k^1 + 7k^2$$

$$\left\{ \begin{array}{c} \Delta c_i^1 \\ \Delta c_i^2 \end{array} \right\} = \frac{L}{24} \left[\begin{array}{cc} \mathcal{H}_j^{11} & \mathcal{H}_j^{12} \\ \mathcal{H}_j^{21} & \mathcal{H}_j^{22} \end{array} \right] \left\{ \begin{array}{c} c_j^1 \\ c_j^2 \end{array} \right\} \tag{11}$$

- Bimolecular

$$\mathcal{K}^{111} = 45k^1 + 11k^2$$

$$\mathcal{K}^{222} = 11k^1 + 45k^2$$

$$\mathcal{K}^{112} = \mathcal{K}^{121} = 11k^1 + 5k^2$$

$$\mathcal{K}^{221} = \mathcal{K}^{212} = 5k^1 + 11k^2$$

$$\mathcal{K}^{122} = 5k^1 + 3k^2$$

$$\mathcal{K}^{211} = 3k^1 + 5k^2$$

$$\mathcal{H}_j^{11} = \mathcal{K}^{111} c_k^1 + \mathcal{K}^{112} c_k^2$$

$$\mathcal{H}_j^{12} = \mathcal{K}^{121} c_k^1 + \mathcal{K}^{122} c_k^2$$

$$\mathcal{H}_j^{21} = \mathcal{K}^{211} c_k^1 + \mathcal{K}^{212} c_k^2$$

$$\mathcal{H}_j^{22} = \mathcal{K}^{221} c_k^1 + \mathcal{K}^{222} c_k^2$$

$$\left\{ \begin{array}{c} \Delta c_i^1 \\ \Delta c_i^2 \end{array} \right\} = \frac{L}{384} \left[\begin{array}{cccc} \mathcal{H}_j^{11} & \mathcal{H}_k^{11} & \mathcal{H}_j^{12} & \mathcal{H}_k^{12} \\ \mathcal{H}_j^{21} & \mathcal{H}_k^{21} & \mathcal{H}_j^{22} & \mathcal{H}_k^{22} \end{array} \right] \left\{ \begin{array}{c} c_j^1 \\ c_k^1 \\ c_j^2 \\ c_k^2 \end{array} \right\} \tag{12}$$

2.4.3 Example: monomolecular-monomolecular reversible reaction $A \rightleftharpoons B$

$$v = k_f c_A - k_b c_B$$

$$R_A = -v$$

$$R_B = v$$

$$\left\{ \begin{array}{c} \Delta c_A^1 \\ \Delta c_B^1 \\ \Delta U^1 \\ \Delta c_A^2 \\ \Delta c_B^2 \\ \Delta U^2 \end{array} \right\} = \left[\begin{array}{cccccc} -H_A^{11} & H_B^{11} & 0 & -H_A^{12} & H_B^{12} & 0 \\ H_A^{11} & -H_B^{11} & 0 & H_A^{12} & -H_B^{12} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ -H_A^{21} & H_B^{21} & 0 & -H_A^{22} & H_B^{22} & 0 \\ H_A^{21} & -H_B^{21} & 0 & H_A^{22} & -H_B^{22} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{array} \right] \left\{ \begin{array}{c} c_A^1 \\ c_B^1 \\ U^1 \\ c_A^2 \\ c_B^2 \\ U^2 \end{array} \right\} \tag{13}$$

with for the forward reaction (replace k by k_f in the formulae!)

$$H_A^{mn} = \frac{L}{24} \mathcal{H}_A^{mn}$$

and for the backward reaction (replace k by k_b in the formulae!)

$$H_B^{mn} = \frac{L}{24} \mathcal{H}_B^{mn}$$

2.5 Poisson's equation

2.5.1 Fluctuation in node

$$\begin{aligned}\Delta U^m &= \int_{L^m} \vec{\nabla}^2 U dL + \int_{L^m} \tfrac{F}{\epsilon} \sum_i z_i c_i dL \\ &= -\int_{\partial L^m} \vec{\nabla} U . d\vec{n} + \sum_i \tfrac{z_i F}{\epsilon} \int_{L^m} c_i dL\end{aligned}$$

2.5.2 Element contribution to fluctuation in node

$$\left\{ \begin{array}{c} \Delta U^1 \\ \Delta U^2 \end{array} \right\} = \left[\begin{array}{cccc} \frac{3L}{8}\frac{z_i F}{\epsilon} & -\frac{\vec{n}^1.\vec{n}^1}{L} & \frac{L}{8}\frac{z_i F}{\epsilon} & -\frac{\vec{n}^1.\vec{n}^2}{L} \\ \frac{L}{8}\frac{z_i F}{\epsilon} & -\frac{\vec{n}^2.\vec{n}^1}{L} & \frac{3L}{8}\frac{z_i F}{\epsilon} & -\frac{\vec{n}^2.\vec{n}^2}{L} \end{array} \right] \left\{ \begin{array}{c} c_i^1 \\ U^1 \\ c_i^2 \\ U^2 \end{array} \right\} \tag{14}$$

2.5.3 Example: binary electrolyte

$$\left\{ \begin{array}{c} \Delta c_A^1 \\ \Delta c_B^1 \\ \Delta U^1 \\ \Delta c_A^2 \\ \Delta c_B^2 \\ \Delta U^2 \end{array} \right\} = \left[\begin{array}{cccccc} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 3Z_A & 3Z_B & n^{11} & Z_A & Z_B & n^{12} \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ Z_A & Z_B & n^{21} & 3Z_A & 3Z_B & n^{22} \end{array} \right] \left\{ \begin{array}{c} c_A^1 \\ c_B^1 \\ U^1 \\ c_A^2 \\ c_B^2 \\ U^2 \end{array} \right\} \tag{15}$$

with

$$Z_i = \frac{L}{8}\frac{z_i F}{\epsilon}$$

$$n^{mn} = -\frac{\vec{n}^m.\vec{n}^n}{L}$$

2.6 Time

2.6.1 Fluctuation in node

$$\Delta c_i^m = \int_{L^m} \frac{\partial c_i}{\partial t} dL$$

2.6.2 Element contribution to fluctuation in node

$$\left\{ \begin{array}{c} \Delta c_i^1 \\ \Delta c_i^2 \end{array} \right\} = \frac{L}{8} \left[\begin{array}{cc} 3 & 1 \\ 1 & 3 \end{array} \right] \left\{ \begin{array}{c} \frac{\partial c_i^1}{\partial t} \\ \frac{\partial c_i^2}{\partial t} \end{array} \right\} \tag{16}$$

3 Boundary element vector

3.1 Electrode reactions

3.1.1 Fluctuation in node

$$R_i = \sum_r s_{i,r} v_r$$

$$v = k_{ox} \exp\left[\frac{\alpha_{ox} nF}{RT}(V-U)\right] c_{red} - k_{red} \exp\left[-\frac{\alpha_{red} nF}{RT}(V-U)\right] c_{ox}$$

$$\Delta c_i^m = R_i^m \tag{17}$$

3.1.2 Example: binary electrolyte, $A \rightleftharpoons B + ne^-$

$$v = k_{ox} \exp\left[\frac{\alpha_{ox} nF}{RT}(V-U)\right] c_B - k_{red} \exp\left[-\frac{\alpha_{red} nF}{RT}(V-U)\right] c_A$$

$$R_A = -v$$

$$R_B = v$$

$$\left\{ \begin{array}{c} \Delta c_A^1 \\ \Delta c_B^1 \\ \Delta U^1 \end{array} \right\} = \left\{ \begin{array}{c} -v \\ v \\ 0 \end{array} \right\} \tag{18}$$

4 Element jacobian

4.1 Convection

Zero contribution.

4.2 Diffusion

Zero contribution (approximately).

4.3 Migration

4.3.1 Element contribution to fluctuation in node

$$\vec{\nabla} U = \frac{\vec{n}^1 U^1 + \vec{n}^2 U^2}{L}$$

$$\left\{ \begin{array}{c} \Delta c_i^1 \\ \Delta c_i^2 \end{array} \right\} = -\frac{\vec{\nabla} U}{16} \cdot \left[\begin{array}{cc} \vec{\mathcal{W}}_i^{11} & \vec{\mathcal{W}}_i^{12} \\ \vec{\mathcal{W}}_i^{21} & \vec{\mathcal{W}}_i^{22} \end{array} \right] \left\{ \begin{array}{c} c_i^1 \\ c_i^2 \end{array} \right\} \tag{19}$$

4.3.2 Example: binary electrolyte

$$\left\{\begin{array}{c}\Delta c_A^1\\ \Delta c_B^1\\ \Delta U^1\\ \Delta c_A^2\\ \Delta c_B^2\\ \Delta U^2\end{array}\right\} = \left[\begin{array}{cccccc}\tilde{M}_A^1 & 0 & 0 & \tilde{M}_A^1 & 0 & 0\\ 0 & \tilde{M}_B^1 & 0 & 0 & \tilde{M}_B^1 & 0\\ 0 & 0 & 0 & 0 & 0 & 0\\ -\tilde{M}_A^1 & 0 & 0 & -\tilde{M}_A^1 & 0 & 0\\ 0 & -\tilde{M}_B^1 & 0 & 0 & -\tilde{M}_B^1 & 0\\ 0 & 0 & 0 & 0 & 0 & 0\end{array}\right]\left\{\begin{array}{c}c_A^1\\ c_B^1\\ U^1\\ c_A^2\\ c_B^2\\ U^2\end{array}\right\} \tag{20}$$

with

$$\tilde{M}_i^{mn} = -\vec{\nabla}U.\frac{\vec{\mathcal{W}}_i^{mn}}{16}$$

4.4 Homogeneous reactions

4.4.1 Element contribution to fluctuation in node

- Monomolecular

Zero contribution (approximately).

- Bimolecular

Because of the symmetry it is the same contribution.

$$\left\{\begin{array}{c}\Delta c_i^1\\ \Delta c_i^2\end{array}\right\} = \frac{L}{384}\left[\begin{array}{cccc}\mathcal{H}_j^{11} & \mathcal{H}_k^{11} & \mathcal{H}_j^{12} & \mathcal{H}_k^{12}\\ \mathcal{H}_j^{21} & \mathcal{H}_k^{21} & \mathcal{H}_j^{22} & \mathcal{H}_k^{22}\end{array}\right]\left\{\begin{array}{c}c_j^1\\ c_k^1\\ c_j^2\\ c_k^2\end{array}\right\} \tag{21}$$

4.5 Poisson's equation

Zero contribution.

4.6 Time

Zero contribution.

5 Boundary element jacobian

5.1 Electrode reactions

5.1.1 Partial derivatives

$$\frac{\partial v}{\partial U} = -\frac{\alpha_{ox}nF}{RT}k_{ox}\exp\left[\frac{\alpha_{ox}nF}{RT}(V-U)\right]c_{red} - \frac{\alpha_{red}nF}{RT}k_{red}\exp\left[-\frac{\alpha_{red}nF}{RT}(V-U)\right]c_{ox}$$

$$\frac{\partial v}{\partial c_{ox}} = -k_{red} \exp\left[-\frac{\alpha_{red} nF}{RT}(V-U)\right]$$

$$\frac{\partial v}{\partial c_{red}} = k_{ox} \exp\left[\frac{\alpha_{ox} nF}{RT}(V-U)\right]$$

$$\left\{\Delta c_i^1\right\} = \left[\begin{array}{cc} \frac{\partial R_i^1}{\partial c_j^1} & \frac{\partial R_i^1}{\partial U^1} \end{array}\right] \left\{\begin{array}{c} c_j^1 \\ U^1 \end{array}\right\} \tag{22}$$

5.1.2 Example: binary electrolyte, $A \rightleftharpoons B + ne^-$

$$\frac{\partial v}{\partial U} = -\frac{\alpha_{ox} nF}{RT} k_{ox} \exp\left[\frac{\alpha_{ox} nF}{RT}(V-U)\right] c_B - \frac{\alpha_{red} nF}{RT} k_{red} \exp\left[-\frac{\alpha_{red} nF}{RT}(V-U)\right] c_A$$

$$\frac{\partial v}{\partial c_A} = -k_{red} \exp\left[-\frac{\alpha_{red} nF}{RT}(V-U)\right]$$

$$\frac{\partial v}{\partial c_B} = k_{ox} \exp\left[\frac{\alpha_{ox} nF}{RT}(V-U)\right]$$

$$\left\{\begin{array}{c} \Delta c_A^1 \\ \Delta c_B^1 \\ \Delta U^1 \end{array}\right\} = \left[\begin{array}{ccc} -\tilde{C}_A^1 & -\tilde{C}_B^1 & -\tilde{U}^1 \\ \tilde{C}_A^1 & \tilde{C}_B^1 & \tilde{U}^1 \\ 0 & 0 & 0 \end{array}\right] \left\{\begin{array}{c} c_A^1 \\ c_B^1 \\ U^1 \end{array}\right\} \tag{23}$$

with

$$\tilde{C}_i^m = \frac{\partial v^m}{\partial c_i^m}$$

$$\tilde{U}^m = \frac{\partial v^m}{\partial U^m}$$